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IMPROVING THE ENVIRONMENTAL SAFETY OF MUNITIONS DISPOSAL BY OB AND OD

by

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INTRODUCTION

Current Situation

Burning and detonating in an open area (OB, OD) and more recently, detonating underground (buried-OD), are the traditional methods for disposing of UXO and surplus or unserviceable energetic materials. Some countries prohibit OB and OD activities entirely and others, such as the U.S., restrict them. In the U.S., the disposal of energetic materials by OB and OD is regulated under Subpart X of Part 264 of the Resource Conservation and Recovery Act1. A Subpart X permit is required to conduct OB and OD because of concerns about: (1) the extent to which the energetic material is converted to innocuous chemicals; (2) the toxicities and dispersion in the environment of the ash, soil and chemical pollutants released; and (3) the blast noise. Because of these concerns the Subpart X permits that have been issued are very restrictive, particularly regarding the quantities that can be destroyed at one time, and over a specified period of time. Unfortunately, at many Subpart X permits require the facility to bury the munitions under one to three meters of soil before they are detonated. While this mitigates the blast noise, as will be shown later in this paper, it increases substantially the quantities of pollutants released.

Hundreds of millions of dollars have been spent in the last fifteen years to develop and test energetic material disposal technologies which are not based on OB or OD processes. Success has been achieved in removing the energetic materials from some items. However, most of the technologies are labor intensive, item specific, and have very limited throughput capacity and relatively high cost. Also, a substantial portion of the recovered energetic materials are still destroyed by OB

processes, either because there are no military or commercial uses for these materials or because the cost to render them commercially salable as energetic materials far exceeds their market value. Thus, for more than 60% of the items in the demil inventory, OB and OD are currently the only disposal technologies available.

The lack of success in finding alternate disposal technologies with wide application and reasonable throughput capacity, the RCRA restrictions and the drawdown of the Armed Forces have combined to cause the demil stockpile to increase by 50,000 to 100,000 tons annually since 1991.

Initial Attempt To Characterize Pollutants Released By OB and OD

In 1984, the U.S. Army initiated a research program to characterize the pollutant emissions from OB and OD activities. In this study helicopters equipped with manual and automated pollutant measurement systems sampled the plumes released when 1 to 5 tons of explosives and propellants were detonated and burned. However, the test results were inconclusive for the following reasons. First, the plume rose too fast for the helicopter to collect a representative sample. Second, the automated and manual samplers were not sensitive enough to measure the pollutant concentrations in the plumes. Third, the plume volume measurement was found to be highly imprecise and subject to operator error.

Comparability of Chamber and Field Test Emission Results

In 1988, the U.S. Army, conducted a workshop in Salt Lake City, UT to address the problems encountered by the earlier study. The workshop participants made the following recommendations. First, sample the plume with a propeller-driven airplane equipped with the appropriate pollutant measurement systems. Second, before conducting any field testing, burn and detonate small quantities of propellants and explosives in the 950 m³ inflatable chamber at Sandia National Laboratories (SNL) in Albuerquerque, NM and determine the identities and concentrations of the compounds emitted. Third, use the results from these chamber studies to select the target analytes for the pollutant measurement systems to be used in the aircraft. Fourth, compare the SNL chamber results to the field detonation and burn results to see if chamber studies provide results equivalent to those from the much more costly field studies.

In 1989-1990, the U.S. Army detonated 225 g quantities of bulk TNT, RDX, Explosive D and Comp B and burned 2 kg quantities of MK6 and a double-based propellant in the SNL chamber. The

pollutant emission factors (the ratio of quantity of a pollutant released to the quantity of the energetic material detonated or burned) obtained in the SNL tests were then compared to those obtained when 900 kg of the explosives were detonated and 3,200 kg of the propellants were burned in the open at Dugway Proving Ground (DPG), UT. The test results showed that the identities and quantities (emission factors) of the compounds released during the chamber detonations and burns were slightly higher, but statistically similar to those from the field tests^{2,3,4}. Although only a very limited number of energetics were tested, the results from all tests showed that OB and OD operations could be an environmentally acceptable way to dispose of energetic materials.

In 1991, the U.S. Army submitted their results to the USEPA with the recommendation that EPA accept emission factors obtained from chamber tests as being equivalent to those that would be obtained from detonating and burning (at ground level) much larger quantities of the same materials. In 1992, EPA concurred with this recommendation.

EPA's concurrence was a major boost to DoD's efforts to determine the emission products from OB and OD activities for it would provided the DoD the opportunity to: (1) characterize ten or more energetic materials at a cost comparable to conducting field tests on one material; (2) collect sufficient sample to meet the minimum quantitation limits of the pollution measurement systems for the target analytes; (3) study the decay rates of the primary and secondary products released from detonations and burns; (4) minimize testing delays due to adverse weather conditions; and (5) obtain the minimum number of detonations and burns required to calculate emission factors on each type of energetic material under repeatable and controlled conditions. This last advantage is very important because it allows one to evaluate the affect that procedural changes have on the emission products released from OB and OD activities.

DoD/EPA Cooperative R&D On Disposal Of Energetic Materials
In 1993, under the sponsorship of the Strategic Environmental
Research and Development Program (SERDP), DoD and EPA began a
cooperative R&D study using detonation and burn chambers to: (1)
compile a comprehensive database of emission factors for the
pollutants released when energetic materials are destroyed by
burning and detonation technologies; and (2) find ways to improve
the environmental safety of these technologies.

To date, two detonation chambers have been used; one located at Dugway Proving Ground, UT and the other at a steel-hardening

facility in Danvers, IL. This paper describes the status of the emission factor database and the results from two special studies to compare the emissions from a buried detonation to those from a surface detonation. One of these studies was done in the DPG BangBox and the other in the Danvers, IL chamber.

DPG EXPERIMENTS

DPG Inflatable Detonation and Burn Test Chamber (BangBox). This 950 m3 chamber is identical to the one at SNL. It sits on a concrete pad and has two sections: an inflatable, 16-m diameter hemisphere (test chamber) made from plastic-coated nylon fabric and a 5.5 x 2.1 x 2.5 m building (airlock) made from plywood. The test chamber is kept inflated by a blower; its volume is maintained at approximately 950 m³ by adjusting a damper at the outlet to the blower. Air is circulated in the test chamber by six fans spaced 60 degrees apart.

The test chamber contains the following pollutant sampling equipment: three high volume samplers for collecting total particulate, metals and selected semivolatile organic compounds (SVOC); three high volume based PM-10 samplers for measuring particles in the inhalable range; and three EPA semi-VOST samplers for collecting selected SVOC and volatile organic compounds (VOC). It also contains a "suppressive shield" (to permit detonating fragment/shrapnel-generating materials in the chamber) constructed from 5.1-cm angle iron and a pollutant gas sampling probe which carries BangBox air to the CO, CO2, NO2 and SO2 automated sampling systems in the airlock. Together, these measurement systems provide the opportunity to analyze the plume for over 300 analytes, including energetics, dioxins and furans.

The maximum net explosive weight (NEW) of energetic material which can be detonated in the test chamber is 225 g and the maximum quantity of PEP which can be burned is 2.2 kg. Materials are burned in a stainless steel pan and detonated either in or suspended over a 1-meter cubed, steel-lined pit. These procedures simulate ground level, unconfined burn and detonation based disposal processes.

Energetic Materials Studied

The emissions from 9 propellants, a propellant manufacturing process waste, 18 explosives and 3 pyrotechnics have been characterized in the DPG BangBox. The propellants, manufacturing waste and 3 pyrotechnics were burned and the explosives were detonated in a normal atmosphere, i.e., 21% oxygen. The pollutants released when diesel-soaked dunnage, a material commonly used to initiate the burning of energetic materials,

were also determined.

The database contains emission factors for the following energetic materials.

Detonation: 20 mm HEI cartridge; 40 mm HEI cartridge; Claymore M18A1 mine; T45E7 adapter booster; signal, illumination, Red Star M 158; signal, illumination, Red Star AN-M43A2; fuze, tail bomb FMU-54 A/B; fuze, tail bomb FMU-139 A/B; flare, IR countermeasure M206; cartridge, impulse, ARD 446-1; cartridge, impulse BBU-36/B; cartridge, impulse, MK 107; gas generator, GGU-A/A; detonating train; detonating cord; tritonal; amatol (50% TNT: 50% ammonium nitrate); composition B; HBX; tritonal (80% TNT: 20% aluminum); tritonal with calcium stearate; and TNT.

Burn: PBXN-110; M-3; M-9; MK-23; M-43; Smokey Sam; smokeless powder (Hercules Unique); manufacturer's waste (aluminized propellant with diesel); and diesel fuel soaked dunnage.

Amatol and tritonal were also used in an experiment intended to assess how detonating oxygen-balanced and oxygen-deficient energetic materials underground affects the emissions (compared to a corresponding ground level detonation). In this experiment amatol and tritonal were detonated while surrounded with 3.6 lbs of water. The water prevented the fireball from forming, something that can happen when an energetic material is detonated deep underground. In this case, the only oxygen available to support the formation of the fireball is the oxygen in the energetic material, itself.

Amatol is an oxygen-balanced explosive, which theoretically contains sufficient oxygen to convert its C, H, and N atoms to CO_2 , $\mathrm{H}_2\mathrm{O}$ and NO_2 , respectively, whereas tritonal is severely oxygen-deficient, i.e., it contains only 12% of the oxygen needed to convert its C, H, and N atoms to these compounds. Amatol and tritonal were selected because they represent two extremes in the oxygen content of commonly used explosives and, also, because they contain the same CO_2 , CO and VOC- generating explosive (TNT). Thus, we could vary the oxygen content of the energetic without having to correct the emission for any CO_2 , CO and VOCs resulting from the material used to vary the oxygen content; CO_2 , CO and VOCs were the primary target analytes in this and the other special study described below (Danvers IL Chamber).

EXPERIMENTS IN THE DANVERS IL CHAMBER

The Danvers, IL chamber is a steel, rectangular-shaped, 70 m³ chamber used in hardening steel casting through an explosive

hardening process. Up to 25 pounds (NEW) of explosive can be detonated in this steel chamber without damaging it - 50 times the DPG BangBox NEW limit.

A set of detonations was done in this chamber using 5 lbs. Of water in a single plastic bag, 40 lbs. of water (equally divided in 10 bags), 40 lbs. of pea gravel and 30 lbs. of $Na_2CO_3:3H_2O_2$ (a solid) either alone or in combination to vary the degree to which the fireball was quenched/inhibited from forming when 5 lbs. of flaked TNT (contained in a plastic bag) was detonated. The more the fireball was quenched, the deeper the buried detonation simulated. The TNT and the other materials were suspended in the chamber approximately equidistant from the top, bottom and sides of the chamber.

When used, the gravel and peroxide surrounded and were in contact with the exterior surface of the bag containing the TNT, and the 5 lbs. of water was 18 inches from the TNT. When the 40 lbs. of water was used, the bags were distributed spherically around the TNT approximately 18 to 24 inches from its center. The series of detonations have been classified as follows: no suppressive materials used (ground level detonation); gravel or peroxide used alone (shallow buried detonation); equal weight of water and TNT used (moderately buried detonation); and gravel/water or peroxide water (deeply buried detonation).

RESULTS

Emission Factor Database

Presently, the database contains emission factors for the 32 items evaluated to date in the DPG BangBox, the four items evaluated in the SNL detonation/burn chamber and the emission factors from the water-suppressed amatol and tritonal The following four types of emission factors are used in the database: (1) uncorrected (no correction for background); (2) corrected for background; (3) average background concentration expressed as an emission factor; and (4) the minimum detection limit for the total sampling system expressed as an emission factor. Users of the database will be able to use the background concentration and the minimum detection limit values to estimate how much the background concentration could have contributed to the emission factor reported for the analyte and the likelihood that the emission factor is meaningful. Ideally, when designing an environmental monitoring plan or conducting a risk assessment, one would prefer to select pollutants which are unique to the OB or OD activities being addressed and occur in concentrations which are measurable.

The database will be submitted to EPA in early May for inclusion in EPA's AP-42 Emission Factor Database. A limited number of copies will also be provided on floppies and CD-ROM diskettes to EPA and DoD employees involved in obtaining or approving Subpart X permits.

The database also contains the following information: chemical and physical composition of the item (where available); description of the sampling and analysis methods used; description of the methods used to calculate the emission factors; an explanation why certain analyte data were not included in the database; and the definition of terms used. In compiling the database, care was taken to clearly identify the following situations: where a sample was not taken; where the background correction yielded a negative emission factor; and where the sample was determined to be either invalid or could not be derived because the information needed to calculate the emission factor was not available.

Emission factors for the following analytes are in the database:

NO2, NO, CO, CO2, HCl, SO2 by automated sampler

HCl, Cl₂ by EPA Method 26

VOCs by canister/GC/MS

VOCs, CO₂, CO by canister/GC/FID

Toxic, heavy metals by Hi-Vol/ICP

SVOC by Hi-Vol/GC/MS

SVOC by Hi-Vol/SFC/MS

SVOC by PS-1/GC/MS

Dioxins by PS-1/GC/MS

Furans by PS-1/GC/MS

PM-10 mass by Hi-Vol type PM-10 sampler.

The following analytes were not included in the database because the measurements were determined to be either invalid or meaningless: toxic, heavy metals by PM-10 sampler; arsenic and mercury by Hi-Vol sampler; O₃; and K, Na and Ca by Hi-Vol and PM-

10 samplers.

The BangBox-derived, emission factor database is now being statistically examined to determine if energetic materials can be classified into "emission product families" based on the chemical composition of the material. This analysis will also determine: (1) if the number of background samples and/or field samples collected for each PEP material can be reduced or should be increased; and (2) if the target analyte list, sampling methods or the sample collection times should be changed.

Effect of Burial on Emission Factors For Detonations.

Table 1 compares the emission factors (normalized to the weight of TNT detonated) for CO2, CO and selected VOC's (acetylene, ethylene, benzene, toluene, and total aromatics) obtained from the standard and water-suppressed amatol and tritonal detonations conducted in the DPG BangBox. As expected, the suppressed detonation, which is equivalent to a deeply-buried detonation, released much higher levels of undesirable pollutants (15 to 500 times higher) than the corresponding ground level detonation. For example, for the tritonal the CO, ethylene and benzene emissions increased by factors of 84, 56 and 530 times, respectively and for the amatol they increased by factors of 60, 60 and 14, respectively. In contrast, the CO2 emissions decreased by a factor of 4 for the tritonal and a factor of 3 for the amatol.

Table 2 compares the emission factors derived from the 5 lb. TNT detonations conducted in the Danvers, IL chamber. The first two rows of the table show the material(s) used to suppress the formation of the fireball and the type of detonation simulated, respectively. Relative to the equivalent surface detonation, the more the fireball is suppressed, the higher the emission factors for CO and the VOCs. For example, the increase in the CO emissions for the three types of burials simulated are: shallow burial (6-fold), moderate burial (18-fold) and deep burial (30-fold). The analogous values for ethylene are 11, 11 and 32 and for benzene they are 24, 78 and 150.

In theory, the 30 lbs. of Interox contained enough oxygen to convert all the C, H and N in the TNT to CO_2 , CO and NO_2 , respectively. However, the similarity between the two shallow burial (equivalent) detonations (gravel vs. Interox) and between the three deep burial (equivalent) detonations, indicates that the presence of the oxygen-rich Interox did not mitigate the increase in the emissions to a noticeable degree. This is consistent with the result from the amatol experiment reported above.

The results in Tables 1 and 2 emphasize that the standard BangBox emission factors, which are equivalent to an unconfined, ground level detonation, should not be used to estimate the emissions from buried detonations, even when the energetic material is oxygen-balanced. They also indicate that burying an oxygen-donating material with the explosive is not a practical means to mitigate the increase in pollutant emissions that results when an energetic is detonated underground rather than at ground level.

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ble 1. Effect of Burial (Simulated with Water) on Tritonal and Amatol Emission Factors (Normalized to New TNT) Table 1.

Explosive Weight (lbs.):				
TNT	0.4	0.25	0.4	0.25
Aluminum	0.1	ı	0.1	1
Ammonium Nitrate	1	0.25	1	0.25
Pounds of Water	0.0	0.0	3.6	3.6
Type Detonation Simulated	Surface	Surface	Deeply Buried	Deeply Buried
Emission Factors:				
CO ₂	1.00	0.45	0.25	0.2
CO ×10²	0.25	0.50	21.0	12.0
Acetylene x104	0.16	0.50	35.0	0.7
Ethylene x104	0.16	0.15	0.6	5.0
Benzene x104	0.03	0.10	1.6	1.4
Toluene x105	0.05	0.35	0.9	6.0
Aromatics x104	0.16	0.20	2.7	2.0

Note: $\rm CO~x10^2~means$ that the actual emission factors for $\rm CO~are~100$ times less than the values in the table, etc.

Table 2. Effect of Burial (Simulated) on Emission Factors From Five-Pound TNT Detonation

Weight (lbs.):							
Gravel	0	0	40	0	40	0	0
Interox	0	30	0	0	0	30	30
Water	0	0	0	Ŋ	40	40	40
Type Detonation Simulated	Surface	Shallow Burial	Shallow Burial	Moderate Burial	Deep Burial	Deep Burial	Deep Burial
Emission Factors:						1.0	
CO ₂	1.3	1.4	ı	6.0	L.	9.0	0.5
CO ×10 ²	8.0	4.8	6.7	16.0	18.0	23.0	28.0
Acetylene x104	6.0	3.4	3.8	2.4	30.0	21.0	25.0
Ethylene x104	0.4	4.6	5.7	4.3	12.0	13.0	17.0
Benzene x104	0.1	2.0	2.8	7.8	14.0	14.0	18.0
Toluene x10 ⁵	0.1	3.3	7.0	13.0	32.0	38.0	48.0
Aromatics x104	0.1	2.5	3.6	9.3	18.0	18.0	23.0
-							

Note: $\rm CO~x10^2$ means that the actual emission factors for $\rm CO~are~100$ times less than the values in the table, etc.